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Digital Twins of a cold-adsorbed Hydrogen tank by Activated Carbons and Metal Organic Frameworks

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Abstract
Hydrogen has the potential to be an important source of clean energy, but the development of efficient and cost-effective methods for storing hydrogen is a key challenge that needs to be addressed in order to make widespread use of hydrogen as an energy source possible. There are different methods for storing hydrogen (i.e. compressed it at high pressures, liquefied by cooling the hydrogen to a temperature of -253°C and stored with a chemical compound), each with its own advantages and disadvantages.
MAST3RBoost (Maturing the Production Standards of Ultraporous Structures for High Density Hydrogen Storage Bank Operating on Swinging Temperatures and Low Compression) is a European project which aims to provide a solid benchmark of cold-adsorbed H2 storage (CAH2) at low compression (100 bar or below) by maturation of a new generation of ultraporous materials for mobility applications, i.e., H2-powered vehicles, including road and railway, air-borne and waterborne transportation. Based on a new generation of Machine Learning-improved ultraporous materials – such as Activated Carbons (ACs) and high-density MOFs (Metal-organic Frameworks) –, MAST3RBoost project will enable a disruptive path to meet the industry goals by developing the first worldwide adsorption-based demonstrator at the kg-scale.
The design of the tank is supported by numerical investigation by means of the use of COMSOL Computational Fluid Dynamic (CFD) code. The model was validated by comparing it against experimental data from Test n. 20 [1], [2], [3], as well as numerical results obtained from the filling process of a 2.5 l tank with activated carbon [4]. A modified Dubinine-Astakhov (MDA) adsorption model is used to describe the adsorption isotherm for MOF and Activated Carbon (AC); the characterization of MOF and AC from simulation point of view is defined by three main MDA parameters: α, β and n_max. In this work a Digital Twin has been developed by the COMSOL Application Builder focused on the effect of different MOF or AC properties on Hydrogen adsorption and temperature inside the tank.
Keywords: Digital Twin, Metal Organic Framework, Activated Carbons, Hydrogen Adsorption, Dubinine-Astakhov equations, Hydrogen Storage.

Introduction
In order to reduce greenhouse gas emissions, using clean and sustainable energy sources is becoming more and more important. In this perspective, hydrogen is a particularly interesting energy source because it can be used to generate heat and power in a clean energy manner. However, one of the main obstacles to hydrogen's widespread use is the scarcity of reliable and safe storage solutions.
There are several methods for storing hydrogen like compressing it at high pressures (350-700 bar), liquefying it by cooling to -253°C or combining it with chemical compound (metal hydrides or hydrocarbons).
Hydrogen can also be adsorbed onto ultraporous materials as a substitute means of storing hydrogen. This method involves physically adsorping hydrogen molecules into the pores of materials including zeolites, activated carbons, and metal-organic frameworks (MOF) that have enormous surface areas and numerous gas-solid interfaces. Compared to compressed hydrogen storage, this technique allows hydrogen to be stored at lower pressures (100 bar) and at higher temperatures (77º K) than liquid hydrogen storage. Furthermore, this adsorption process requires lower temperatures and allows for faster absorption than chemical hydrogen storage.

A digital twin is a virtual model of a system designed to mirror its physical counterpart. Once the methods for hydrogen storage have been studied, the tank has been designed and the numerical simulation model has been validated [3] [5], the Digital Twin developed in this paper represents a tool able to help with the tank design optimization in different filling configurations. It will optimize the process by focusing on the effect of different MOF or AC properties on Hydrogen adsorption, temperature and pressure swing inside the tank and the power and energy generated during the charging process.

Tank geometry and default data
The tank model in the released Digital Twin features a simplified axial symmetrical geometry, designed to accelerate the simulation process for evaluating the adsorption performance of various ACs and MOFs.

In the validated COMSOL model the tank is defined by the following geometrical and material properties:

***Table 1**: Tank properties*

Volume	2,4946 l
Diameter	0,1 m
Height	0,4 m
Hole area	$5{,}0265*10^{-5}$ m^2
Material	Steel AISI 4340

The application default data are validated in [5].
In the future, the model will be enhanced with a more complex geometry to more closely resemble the actual prototype that will be constructed.

Digital Twin Preview

The Digital Twin presented in this article is developed using the Application Builder module within the COMSOL Multiphysics® platform. This module includes a complete set of user interface, programming, and debugging tools for creating custom applications. COMSOL apps are custom-made simulation tools that retain all the advantages of a model built with the Model Builder, without the extraneous information. The app user will be focused only on the relevant input parameters and computational results, without requiring foreknowledge of the underlying model.

The application interface is divided in two sections: Input and Output:

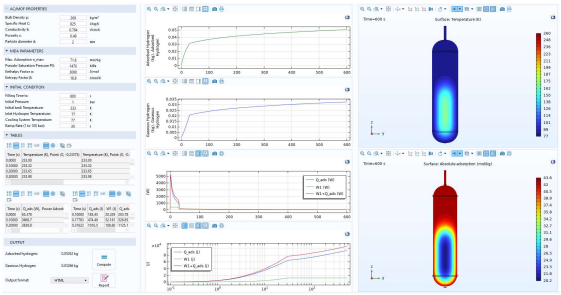

Figure 1. Digital Twin application interface

Input

In this section the user can change some properties related to:
- ACs/MOF Properties:

***Table 2**: ACs/MOF Properties: editable default variables*

	ACs	MOF
Bulk Density ρ [kg/m³]	269	409
Specific Heat C [J/(kg*K)]	825	742.5
Conductivity k [W/(m*K)]	0.764	0.3
Porosity ε	0.49	0.1266
Particle Diameter d [mm]	2	2

- MDA Parameters: the modified Dubinine-Astakhov (MDA) adsorption model is used to describe the adsorption isotherm for ACs and MOF. The absolute adsorption is given by the following equation [5]:

$$n_a = n_{max}\exp\left[-\left(\frac{RT}{\alpha_{D-A}+\beta_{D-A}T}\ln\frac{p_0}{p}\right)^m\right]$$

Where R is the universal gas constant, T and p are the temperature and pressure, respectively.

***Table 3**: MDA Parameters: Editable default variables*

	ACs	MOF
Maximum Adsorption n_{max} [mol/kg]	71.6	70.178
Pseudo-Saturation Pressure P0*[1] [MPa]	1470	1927
Enthalpy Factor α [J/mol]	3080	2541.5
Entropy Factor β [J/mol*k]	18.9	8.0691

*[1]: P0 is usually 1470 for ACs and 1927,3 MPa for MOF [5].

- Initial Condition:

***Table 4**: Initial Condition: Editable variables*

	ACs/MOF
Filling Time [s]	600
Initial Pressure [bar]	1
Initial Tank Temperature [K]	233
Inlet Hydrogen Temperature [K]	77
Cooling System Temperature*[2] [K]	77
Ramp Rate (time to reach 100 bar) [s]	30

*[2]: As this geometry does not foresee any heat exchanger inside the tank the cooling system is represented by the temperature outside the surface of the tank

Output

- Tables:

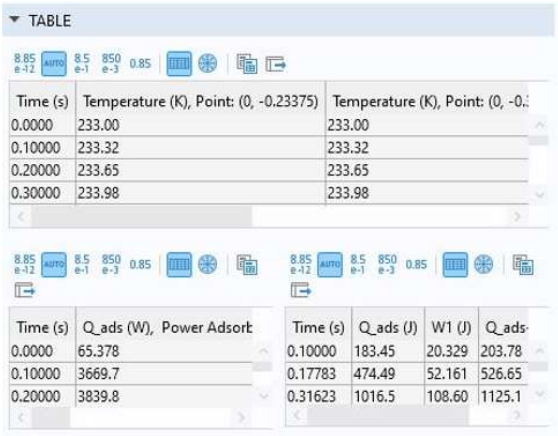

Figure 2. DT tables

During the simulation the tables will report updated result for:

▪ Temperature [K] detected in four points as indicated in figure 3 and table 5, adsorbed hydrogen [kg], gaseous hydrogen [kg], inlet flow [kg/s] and volume [m^3]. All these values are returned as a function of time: every 0.1 second until the ramp rate is reached, then every second.

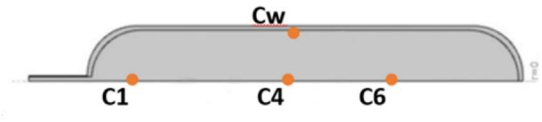

Figure 3. Monitor point locations

***Table 5**: Monitor point coordinates*

Point	r	z
C1	0.00 m	-0.09875 m
C4	0.00 m	-0.23375 m
C6	0.00 m	-0.32375 m
Cw	0.0469 m	-0.23375 m

▪ Heat generated by the hydrogen adsorption Q_ads, work generated by compression W1 and the sum of these two parameters W1+Q_ads in terms of power [W]. All these values are returned as a function of time: every 0.1 second until the ramp rate is reached, then every second;

▪ Heat generated by the hydrogen adsorption Q_ads, work generated by compression W1 and the sum of these two parameters W1+Q_ads in terms of Energy integrated in function of time [J]. All these values are returned as a logarithmic function of time.

Data tables can be exported in .txt, .csv or .dat file format.

- Output:

Figure 4. DT output

In this section is visible the *Compute* button that initialize the elaboration process. At the end of the simulation in this section will be displayed the value of the adsorbed and gaseous hydrogen [kg]. Moreover, the user can export the data generated in html or Microsoft Word format with the *Report* button.

- Graphs:

At the end of the simulation the linear graphs for the adsorbed hydrogen, gaseous hydrogen, power and energy in function of the time and the surface graphs for the temperature and the absolute adsorption will be updated.

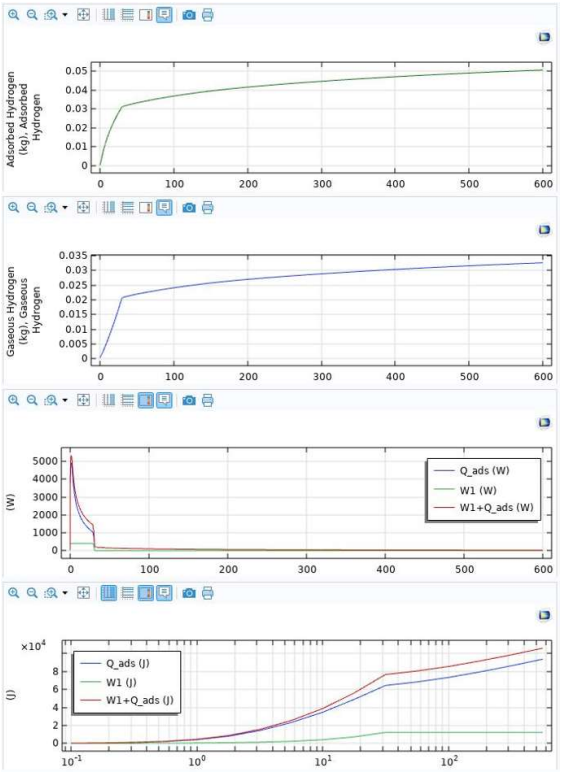

Figure 5. DT linear graphs

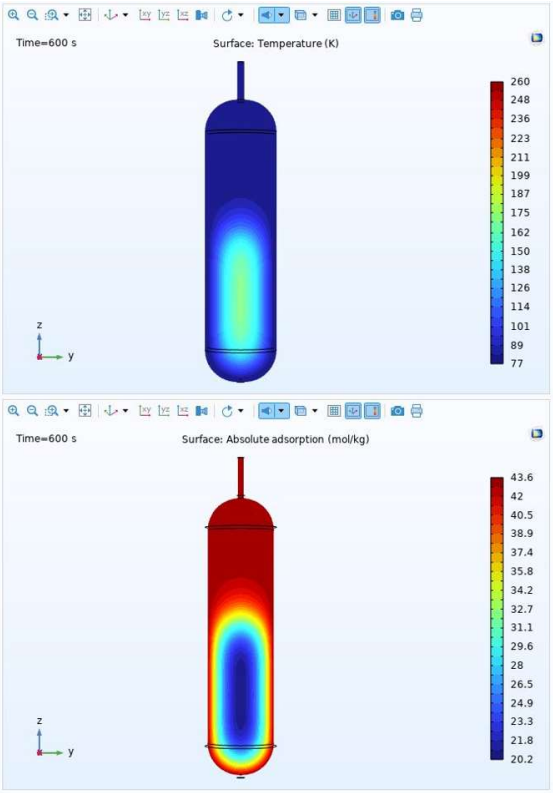

Figure 6. DT surface graphs

ACs and MOF simulations by Digital Twin

The app allows users to modify properties of ACs and MOFs, such as the maximum adsorption n_{max}, the enthalpy factor α, the entropy factor β, and the pseudo-saturation pressure P0. Starting from the default data, the simulation was recalculated by adjusting only the values corresponding to the MDA parameters. The parameters have been replaced with ACs values under development at the University of Nottingham.

Simulation 1 - Parameters changed ACs – CS2-A1 developed by University of Nottingham:
nmax: 106.73 mol/kg, enthalpy factor α: 6116.24 J/mol, entropy factor β: 36.02 J/molK

% Time (s)	Temperature (K), Point C1	Temperature (K), Point C2	Temperature (K), Point C3	Temperature (K), Point C4
0	233	233	233	233
30	78	100	378	79
100	77	94	378	77
200	77	92	356	77
300	77	89	309	77
400	77	87	259	77
500	77	85	216	77
600	77	83	184	77

% Time (s)	Adsorbed Hydrogen (kg)	Gaseous Hydrogen (kg)	Volume (m^3)	Inlet flow (kg/s)
0	0,0279	0,0003	0,0025	0,00003
30	0,1045	0,0229	0,0025	0,00147
100	0,1100	0,0260	0,0025	0,00009
200	0,1142	0,0285	0,0025	0,00005
300	0,1169	0,0302	0,0025	0,00004
400	0,1188	0,0315	0,0025	0,00003
500	0,1204	0,0326	0,0025	0,00002
600	0,1216	0,0335	0,0025	0,00002

Figure 7. Data table

Adsorbed Hydrogen: 0.1216 kg
Gaseous Hydrogen: 0.03351 kg

Initial condition changes simulation by Digital Twin

As reported in the previous paragraph, starting from the default data, the simulation has been recalculated by modifying only the values related to the initial condition like the filling time, the initial pressure, the initial tank temperature, the inlet hydrogen temperature, the cooling system temperature and the ramp rate.

Simulation 2 - Parameters changed (ACs default data): filling time 300 s, initial pressure 3 bar, initial tank temperature 77 K, inlet hydrogen temperature 288 K, cooling system temperature 77 K and ramp rate 25 s

% Time (s)	Temperature (K), Point C1	Temperature (K), Point C2	Temperature (K), Point C3	Temperature (K), Point C4
0	77	77	77	77
25	292	113	113	78
50	289	113	113	78
100	281	115	113	77
150	271	118	113	77
200	258	121	113	77
250	244	123	112	77
300	231	125	111	77

% Time (s)	Adsorbed Hydrogen (kg)	Gaseous Hydrogen (kg)	Volume (m^3)	Inlet flow (kg/s)
0	0,0227	0,0015	0,0025	-0,44329
30	0,0364	0,0232	0,0025	0,00086
100	0,0379	0,0242	0,0025	0,00008
200	0,0398	0,0254	0,0025	0,00006
300	0,0414	0,0264	0,0025	0,00005
400	0,0427	0,0272	0,0025	0,00004
500	0,0438	0,0280	0,0025	0,00003
600	0,0448	0,0286	0,0025	0,00003

Figure 8. Data Table

Adsorbed Hydrogen: 0.04482 kg
Gaseous Hydrogen: 0.02861 kg

Power and Energy simulation by Digital Twin

The Digital Twin allows to extrapolate the power and energy generated of the previous simulations.

Simulation 1 - Parameters changed ACs – CS2-A1 developed by University of Nottingham:
nmax: 106.73 mol/kg, enthalpy factor α: 6116.24 J/mol, entropy factor β: 36.02 J/molK

% Time (s)	Q_ads (W), Adsorbed Hydrogen Power	W1 (W), Compression Hydrogen Power	W1+Q_ads (W)
0,1	93448	373	93821
0,2	93642	459	94101
0,3	76527	443	76970
0,6	51586	417	52003
1	37768	410	38178
1,8	24470	407	24876
3,2	14229	406	14635
5,6	7952	405	8357
10	4277	405	4683
17,8	2234	405	2640
32	213	0	213
56	146	0	146
100	105	0	105
178	63	0	63
316	37	0	37
562	18	0	18

Figure 9. Power table

% Time (s)	Q_ads (J), Adsorbed Hydrogen Energy	W1 (J), Compression Hydrogen Energy	Q_ads+W1 (J)
0,1	4772	18	4789
0,2	12184	49	12233
0,3	23985	112	24097
0,6	39370	217	39587
1,0	58910	398	59308
1,8	82550	715	83265
3,2	108584	1277	109862
5,6	134557	2275	136833
10,0	159695	4050	163745
17,8	183562	7205	190767
31,6	203674	12222	215896
56,2	208002	12222	220225
100,0	213478	12222	225701
177,8	219753	12222	231975
316,2	226474	12222	238696
562,3	232934	12222	245156

Figure 10. Energy Table

Use of Digital Twin

COMSOL users can run this Digital Twin within COMSOL Multiphysics. Additionally, COMSOL applications can be made accessible to users who do not have COMSOL Multiphysics by compiling them into standalone applications using COMSOL Compiler™ or by allowing access through a COMSOL Server™ installed on a network or in the cloud. Users can then run these applications freely, either as standalone programs, on a COMSOL Server via a web browser, or through a COMSOL Client.

Conclusions

The Digital Twin presented in this article is aimed to be a tool that has the potential to be transformed into a commercial product suitable for different and more complex tank geometries. Moreover, this application can simulate the influence of different MOF or ACs properties and simulate various initial conditions on hydrogen adsorption, temperature and pressure swing giving as output the power and energy generated during the charging process. Therefore, the Digital Twin represents a tool able to help with the tank and auxiliaries design and optimization at different temperature and pressure swing for complex tank geometries

References

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